Accuracy and efficiency of modern methods for electronic structure calculation on heavy- and superheavy-element compounds

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The methods which are actively used for electronic structure calculations of low-lying states of heavy- and superheavy-element compounds are briefly described. The advantages and disadvantages of the Dirac-Coulomb-Breit Hamiltonian, Huzinaga-type potential, shape-consistent Relativistic Effective Core Potential (RECP) and Generalized RECP are discussed. The nonvariational technique of the electronic structure restoration in atomic cores after the RECP calculation of a molecule is presented. The features of the approaches accounting for electron correlation, the configuration interaction and coupled cluster methods, are also described. The results of calculations on E113, E114, U and other heavy-atom systems are presented.

I. INTRODUCTION

High-precision calculations of molecules with heavy and superheavy atoms that provide "chemical accuracy" (1 kcal/mol or 350 cm^{-1}) for excitation and dissociation energies of low-lying states are extremely time-consuming. Employing the latest theoretical and program developments is necessary on the following stages:

(A) selection of an effective spin-dependent Hamiltonian;

(B) basis set optimization;

(C) appropriate way of accounting for correlation.

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In order to minimize the computational efforts necessary to provide a given accuracy in calculation of properties, it is important to achieve the equivalent (balanced) level of accuracy in each of these stages in the most economical way. Moreover, too high accuracy which can be formally attained at the first two stages by, e.g., *(a)* employing an effective Hamiltonian, in which inactive core electrons are treated explicitly or/and *(b)* using a too large basis set etc. can result in abnormal requirements to computers at the last stage.

In the present paper, the main attention is paid on items (A) and (C). The Dirac-Coulomb-Breit (DCB) Hamiltonian and the Relativistic Effective Core Potential (RECP) method which are widely employed [at stage (A)] are described in sections II and III. The Configuration Interaction (CI) and Coupled Cluster (CC) methods which are most popular in correlation calculations, [at stage (C)] are presented in sections IV and V. In opposite to the density functional approaches, the CI and CC methods allows one to study excited electronic states of a given symmetry with high level of accuracy.

II. DIRAC-COULOMB(-BREIT) HAMILTONIAN

It is well known that the Dirac-Coulomb (DC) Hamiltonian with the Breit interaction and other Quantum ElectroDynamic (QED) corrections taken into account provide a very high accuracy of calculations of heavy atoms and heavy-atom molecules. The DC Hamiltonian has the form (in atomic units $e = m = \hbar = 1$, where e and m are the electron charge and mass, $\hbar$ is Planck constant):

$$\mathbf{H}^{\rm DC} \;=\; \sum_p \mathbf{h}^{\rm D}(p) + \sum_{p>q} \frac{1}{r_{pq}} \;, \tag{1}$$

where indices p, q run over all the electrons in an atom or molecule, r_{pq} is the distance between electrons p and q, and the one-electron Dirac operator $\mathbf{h}^{\rm D}$ is

$$\mathbf{h}^{\rm D} \;=\; c(\vec{\alpha}\cdot\vec{p}) + mc^2(\beta - 1) + V^{\rm nuc} \;, \tag{2}$$

c is the speed of light, $V^{\rm nuc}$ is the nuclear potential including the effect of finite nuclear size etc., $\vec{p}{=}-i\vec{\nabla}$ is the electron momentum operator, $\vec{\alpha}, \beta$ are the $4{\times}4$ Dirac matrices.

The lowest-order QED correction includes the interelectronic exchange by one transverse photon. In the Coulomb gauge, it leads to so-called Dirac-Coulomb-Breit Hamilto-

nian,

$$\mathbf{H}^{\mathrm{DCB}} \;=\; \mathbf{H}^{\mathrm{DC}} + \sum_{p>q} B_{pq} \;, \tag{3}$$

where

$$B_{pq}(\omega_{pq}) = -(\vec{\alpha}_p\cdot\vec{\alpha}_q)\frac{\cos(\omega_{pq}r_{pq})}{r_{pq}} + (\vec{\alpha}_p\cdot\vec{\nabla}_p)(\vec{\alpha}_q\cdot\vec{\nabla}_q)\frac{\cos(\omega_{pq}r_{pq})-1}{\omega_{pq}^2 r_{pq}} \;, \tag{4}$$

ω_{pq} designates the frequency of the photon exchanged between electrons p and q. A low-frequency expansion of the cosines yields the incomplete Breit interaction $B_{pq}(0)$:

$$B_{pq}(0) \;=\; -\vec{\alpha}_p\cdot\vec{\alpha}_q/r_{pq} \;+\; \frac{1}{2}\left[\vec{\alpha}_p\cdot\vec{\alpha}_q - (\vec{\alpha}_p\cdot\vec{r}_{pq})(\vec{\alpha}_q\cdot\vec{r}_{pq})/r_{pq}^2\right]/r_{pq} \;. \tag{5}$$

These terms describe the instantaneous magnetostatic interaction and classical retardation of the electric interaction between electrons. The contribution from the first term (called Gaunt interaction) to transition energies and hyperfine structure (HFS) constants can be observed in atomic Dirac-Hartree-Fock (DHF) calculations (tables I and II).

The one-electron basis functions in calculations with the DC(B) Hamiltonian are the four-component Dirac spinors. The DC(B)-based calculations have the following disadvantages:

- too many electrons are treated explicitly in heavy-atom systems and too large basis set of Gaussians is required for accurate description of the large number of oscillations which valence spinors have in the case of a heavy atom;

- the necessity to work with the four-component Dirac spinors leads to serious complication of calculations as compared to the nonrelativistic case.

III. RELATIVISTIC EFFECTIVE CORE POTENTIALS

In calculations on heavy-atom molecules, the DC and DCB Hamiltonians are usually replaced by an effective Hamiltonian

$$\mathbf{H}^{\mathrm{Ef}} \;=\; \sum_{p_v}[\mathbf{h}^{\mathrm{Schr}}(p_v) + \mathbf{U}^{\mathrm{Ef}}(p_v)] + \sum_{p_v>q_v}\frac{1}{r_{p_v q_v}} \;, \tag{6}$$

written only for valence or "valence-extended" (when some outermost core shells are treated explicitly) subspace of electrons denoted by indices p_v and q_v; $\mathbf{U}^{\mathrm{Ef}}$ is an RECP

operator simulating, in particular, interactions of the explicitly treated electrons with those which are excluded from the RECP calculation. In Eq. (6),

$$\mathbf{h}^{\rm Schr} = -\frac{1}{2}\vec{\nabla}^2 + V^{\rm nuc} \tag{7}$$

is the one-electron operator of the nonrelativistic Schrödinger Hamiltonian. Contrary to the four-component wave function used in DC(B) calculations, the pseudo-wave function in the RECP case can be both two- and one-component.

A. Huzinaga-type potential

When forming chemical bonds in heavy-atom molecules, states of core electrons are practically unchanged. To reduce computational efforts in expensive molecular calculations, the "frozen core" approximation is often employed.

In order to "freeze" core (c) spinors, the energy level shift technique can be applied. Following Huzinaga, *et al.* [1], one should add the matrix elements of the Hartree-Fock (HF) field operators, the Coulomb ($\mathbf{J}$) and spin-dependent exchange ($\mathbf{K}$) terms, over these core spinors to the one-electron part of the Hamiltonian together with the level shift terms as the effective core operator $\mathbf{U}^{\rm Ef}_{\rm Huz}$:

$$\mathbf{U}^{\rm Ef}_{\rm Huz} = (\mathbf{J}-\mathbf{K})[\varphi_{n_c lj}] + \sum_{n_c,l,j} B_{n_c lj}\ |\varphi_{n_c lj}\rangle\langle\varphi_{n_c lj}| \quad (\text{i.e. } \varepsilon_{n_c lj} \to \varepsilon_{n_c lj}+B_{n_c lj})\ , \tag{8}$$

where n_c, l and j are the principal, orbital momentum and total momentum quantum numbers, the $B_{n_c lj}$ parameters are at least of order $|2\varepsilon_{n_c lj}|$ and $\varepsilon_{n_c lj}$ is the one-electron energy of the core spinor $\varphi_{n_c lj}$ that is frozen. Such nonlocal terms are needed in order to prevent collapse of the valence electrons to the frozen core states. As it will be shown below, all the terms with the frozen core spinors (the level shift operator and exchange interactions) can be transformed to the spin-orbit representation in addition to the spin-independent Coulomb term.

B. Shape-consistent radially-local RECPs

In other RECP versions, the valence spinors are smoothed in the core regions. Consider the shape-consistent radially-local (or semi-local) RECP developed by K. Pitzer's group [2,

3]. The nodeless numerical pseudospinors $\widetilde{\varphi}_{n_v lj}(r)$ are constructed of the large components $P_{n_v lj}(r)$ of the valence (v) DHF spinors (one pseudospinor for each l and j):

$$\widetilde{\varphi}_{n_v lj}(r) = \begin{cases} P_{n_v lj}(r) \ , & r \geq R_c \ , \\ f(r) = r^{\gamma} \sum_{i=0}^{5} a_i r^i, & r < R_c \ , \end{cases} \tag{9}$$

where r is the distance between the nucleus and electron. The matching (or core) radius, R_c, is chosen near the outermost extremum for the large component and the a_i coefficients are taken such that the pseudospinors are smooth and nodeless. The power γ is typically chosen higher than $l+1$ to ensure an efficient ejection of the valence electrons from the core region.

To derive the RECP components U_{lj}, the HF equations are inverted for the valence pseudospinors so that $\widetilde{\varphi}_{n_v lj}$ become solutions of the nonrelativistic-type HF equations (but with j-dependent potentials) for a "pseudoatom" with removed core electrons [4]:

$$U_{lj}(r) = \widetilde{\varphi}^{-1}_{n_v lj}(r) \Big(\frac{1}{2}\frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} + \frac{Z^*}{r} - \widetilde{\mathbf{J}}(r) + \widetilde{\mathbf{K}}(r) + \varepsilon_{n_v lj} \Big) \widetilde{\varphi}_{n_v lj}(r) \ , \tag{10}$$

where $Z^* = Z - N_c$, Z is the nuclear charge, N_c is the number of excluded core electrons, $\widetilde{\mathbf{J}}$ and $\widetilde{\mathbf{K}}$ are the Coulomb and exchange operators on the pseudospinors $\widetilde{\varphi}_{n_v lj}$, $\varepsilon_{n_v lj}$ are their one-electron energies (the same as for the original spinors).

The radially-local RECP operator $\mathbf{U}^{\rm Ef}_{\rm rloc}$ can be written in the form:

$$\mathbf{U}^{\rm Ef}_{\rm rloc} = \frac{N_c}{r} + U_{LJ}(r) + \sum_{l=0}^{L} \sum_{j=|l-1/2|}^{l+1/2} [U_{lj}(r) - U_{LJ}(r)] \mathbf{P}_{lj} \ , \quad \mathbf{P}_{lj} = \sum_{m_j=-j}^{j} |ljm_j\rangle\langle ljm_j| \ , \tag{11}$$

where $J = L + 1/2$, $L = l_c^{max} + 1$ and l_c^{max} is the highest orbital momentum of the core spinors, m_j is the projection of the total momentum.

Using the identities for the $\mathbf{P}_{lj}$ projectors [5]:

$$\mathbf{P}_{l,j=l\pm 1/2} \ = \ \frac{1}{2l+1} \Big[\Big(l + \frac{1}{2} \pm \frac{1}{2} \Big) \mathbf{P}_l \pm 2 \mathbf{P}_l \ \vec{\mathbf{l}} \cdot \vec{\mathbf{s}} \ \mathbf{P}_l \Big] \ , \quad \mathbf{P}_l = \sum_{m_l=-l}^{l} |lm_l\rangle\langle lm_l| \ . \tag{12}$$

the RECP operator can be rewritten in the spin-orbit representation, where $\vec{\mathbf{l}}$ and $\vec{\mathbf{s}}$ are operators of the orbital and spin momenta, m_l is the projection of the orbital momentum.

Similar to Huzinaga-type potentials, the shape-consistent radially-local RECPs allows one to exclude chemically inactive electrons already from the RECP/SCF stage of calculations. Moreover, they have the following advantages:

⋆ The oscillations of the explicitly treated spinors are smoothed in the core regions of heavy atoms when generating nodeless pseudospinors. Therefore, the number of the one-electron Gaussian basis functions may be minimized, thus reducing dramatically both the number of two-electron integrals and the computational time.

⋆ The small components of the four-component spinors are eliminated and the non-relativistic kinetic energy operator is used. The RECP method allows one to use a well-developed nonrelativistic technique of calculation and relativistic effects are taken into account with the help of spin-dependent semi-local potentials. Breit and other two-electron QED interactions can be efficiently treated within the one-electron RECPs.

⋆ In principle, correlations of the explicitly treated electrons with those which are excluded from the RECP calculation can be considered within "correlated" RECP versions. Reducing the number of explicitly correlated electrons with the help of the correlated RECPs is a very promising way to minimize efforts when performing high-precision molecular calculations.

The disadvantages of the semi-local RECPs are:

- By now, different versions of the radially-local RECPs provide a comparable level of accuracy for the same number of the explicitly treated electrons. It is clear that the explicit inclusion of the outer core electrons into the RECP calculation is the way to increase the accuracy. However, the extension of the space of these electrons more than some limit does not improve the accuracy as is obtained in all our calculations with RECPs. The RECP errors still range up to 1000–3000 cm^{-1} and more even for the dissociation of the lowest-lying states and for energies of transition between them.

- The reliability of the radially-local RECP versions is not high for transitions with the excitations in d, f-shells in transition metals, lanthanides, actinides, etc.

- Moreover, the direct calculation of such properties as electronic densities near heavy nuclei, HFS, and matrix elements of other operators singular on heavy nuclei is impossible as a result of smoothing the spinors in the core regions of heavy elements.

To overcome the above disadvantages, the Generalized RECP (GRECP) method (see subsection III C) and the One-Center Restoration (OCR) procedures (see subsection III D) were developed.

C. Generalized RECP

It was shown in paper [6] that a requirement for pseudospinors to be nodeless is not necessary to generate the shape-consistent RECP components. In the case of pseudospinors with nodes, the RECP components are singular because division by zero appears in Eq. (10). This problem is overcome in the GRECP method by interpolating the potentials in the vicinity of these nodes. It was shown both theoretically and computationally that the interpolation errors are small enough. This allows one to generate different potentials, U_{n_clj} and U_{n_vlj}, for outer core and valence pseudospinors, unlike the conventional RECP approach.

The GRECP operator is written in the form [7]:

$$\begin{aligned}
\mathbf{U}^{GRECP} &= \frac{N_c}{r} + U_{n_vLJ}(r) + \sum_{l=0}^{L} \sum_{j=|l-1/2|}^{l+1/2} [U_{n_vlj}(r) - U_{n_vLJ}(r)]\mathbf{P}_{lj} \\
&+ \sum_{n_c} \sum_{l=0}^{L} \sum_{j=|l-1/2|}^{l+1/2} \Big\{ [U_{n_clj}(r) - U_{n_vlj}(r)]\widetilde{\mathbf{P}}_{n_clj} + \widetilde{\mathbf{P}}_{n_clj}[U_{n_clj}(r) - U_{n_vlj}(r)] \Big\} \\
&- \sum_{n_c,n_c'} \sum_{l=0}^{L} \sum_{j=|l-1/2|}^{l+1/2} \widetilde{\mathbf{P}}_{n_clj} \Big[\frac{U_{n_clj}(r) + U_{n_c'lj}(r)}{2} - U_{n_vlj}(r) \Big] \widetilde{\mathbf{P}}_{n_c'lj}, \qquad (13)
\end{aligned}$$

$$\widetilde{\mathbf{P}}_{n_clj} = \sum_{m_j=-j}^{j} |n_c\widetilde{ljm_j}\rangle\langle n_c\widetilde{ljm_j}| \ .$$

The new non-local terms (the second and third lines in the above equation) were added to the conventional semi-local RECP operator. These terms take into account the difference between the effective potentials acting on the outer core and valence electrons with the same l and j quantum numbers.

The GRECP method allows one to improve accuracy of calculations by regular manner when including more outer core shells explicitly into the GRECP calculations. More details on the GRECP method can be found in [8, 9]. To compare different effective potential versions by accuracy, we carried out both all-electron calculations with the DC Hamiltonian and calculations with RECPs of different groups. The RECP errors in

reproducing the DHF all-electron results are studied in [8, 9] etc. One can see from our atomic HF calculations [10] and correlation calculations on the Hg [11] and Pb [12] atoms, that the accuracy of the GRECP is up to an order of magnitude higher than that of the other tested RECPs even for the cases when the same number of only outermost core shells is treated explicitly.

Results for the eka-thallium atom (E113) are presented in table III. The GRECP errors are collected into two groups. The errors for transitions without change in the occupation number of the $6d$ shell are rather small. The errors for transitions with change in the occupation number of the $6d$ shell are about 400 cm^{-1}. The latter errors have a systematic nature and are connected with the fact that the $6d$ shell in the present GRECP version is described with the help of nodeless pseudospinors. Of course, these errors can be reduced significantly if one includes the $5d$ electrons explicitly in the GRECP calculations. The Self-Consistent (SfC) RECP method was suggested in [8, 13], it allows one to minimize the above mentioned errors without extension of space of explicitly treated electrons. New terms with an operator of the occupation number of the outermost d (or f) shell are added to the RECP operator. This method is most optimal for studying compounds of transition metals, lanthanides, and actinides. The comparison of accuracy of different RECP versions in calculations on the uranium atom can be found in table IV and in papers [8, 13].

D. Nonvariational One-Center Restoration of electronic structure in cores of heavy-atoms in a molecule (NOCR)

In the valence region, the electronic density obtained from the two-component GRECP (pseudo)wave function very accurately reproduces the corresponding all-electron four-component density. In the core region, the pseudospinors are smoothed, so that the electronic density with the (pseudo)wave function is not correct.

The following restoration scheme was developed (see [14, 15] and references):

- Generation of equivalent basis sets of atomic (one-center) four-component spinors $\left\{ \begin{pmatrix} f_{nlj}(r)\chi_{ljm_j} \\ g_{nlj}(r)\chi_{l'jm_j} \end{pmatrix} \right\}$ (where f_{nlj}, g_{nlj} are the radial parts, χ_{ljm_j} are the spin-angular parts of the atomic Dirac spinors and $l'=2j-l$) and two-component pseudospinors

$\{\tilde{f}_{nlj}(r)\chi_{ljm_j}\}$ by atomic finite-difference (numerical) all-electron DHF and two-component GRECP/HF calculations of the same valence configurations of the atom and its ions.

- The molecular pseudospinorbitals $\tilde{\phi}_i$ are then expanded in the basis set of the one-center two-component atomic pseudospinors (for $r \leq R_c^{\rm rest}$, where $R_c^{\rm rest} \geq R_c$),

$$\tilde{\phi}_i(\mathbf{x}) \approx \sum_{l=0}^{L_{max}} \sum_{j=|l-1/2|}^{l+1/2} \sum_{n,m_j} c^i_{nljm_j} \tilde{f}_{nlj}(r)\chi_{ljm_j} \ , \tag{14}$$

where $\mathbf{x}$ denotes spatial and spin variables.

- Finally, the atomic two-component pseudospinors are replaced by the equivalent four-component spinors in the molecular basis and the expansion coefficients $c^i_{nljm_j}$ from Eq. (14) are preserved:

$$\phi_i(\mathbf{x}) \approx \sum_{l=0}^{L_{\rm max}} \sum_{j=|l-1/2|}^{l+1/2} \sum_{n,m_j} c^i_{nljm_j} \begin{pmatrix} f_{nlj}(r)\chi_{ljm_j} \\ g_{nlj}(r)\chi_{l'jm_j} \end{pmatrix} \ . \tag{15}$$

The molecular four-component spinors constructed this way are orthogonal to the inner core spinors of the heavy atom, as the atomic basis functions used in Eq. (15) are generated with the inner core electrons treated as frozen. The properties described by the operators singular close to (heavy) nuclei are calculated with the restored bispinors ϕ_i . More advanced technique of the variational restoration is proposed in [15].

IV. CONFIGURATION INTERACTION

The many-electron wavefunction Ψ^{CI} in the CI method is presented by a linear combination of determinants D_I

$$\Psi^{CI} = \sum_I C_I^{CI} D_I \ , \tag{16}$$

C_I^{CI} are some numbers (CI coefficients). In turn, each N-electron determinant is an anti-symmetric production of N one-electron basis functions where N is the number of electrons in the considered system. The CI equations are written as

$$\sum_J H_{IJ} C_J^{CI} = E^{CI} C_I^{CI} \ , \tag{17}$$

where H_{IJ} are Hamiltonian matrix elements in the basis set of the determinants and E^{CI} is the CI energy. To find the coefficients and the energy in the CI method, one should diagonalize the Hamiltonian matrix.

If all possible determinants are considered then the method (called Full-CI) will provide the "exact" solution in the framework of a given one-electron basis set and an employed Hamiltonian. However, requirements to the computational resources in the Full-CI case are usually so huge that such calculations are practically impossible for systems of interest except the cases of very small numbers of correlated electrons and basis functions. In almost all the CI calculations, only some selected (the most important) determinants are explicitly considered. To take into account the effect of the unselected determinants, various semi-empirical corrections (e.g., the Davidson correction [16]) can be employed. In precise calculations, the number of selected determinants reaches a few millions and more, therefore a very large Hamiltonian matrix should be diagonalised. The iterative diagonalization (Davidson) method is then used to obtain a few low-lying roots of this matrix.

There are two main categories of the CI method [17]:

- "Conventional CI": the Hamiltonian matrix elements are calculated once and saved in memory,
- "Direct CI": only those Hamiltonian matrix elements are calculated at each step of the diagonalization procedure which are required at the moment.

The CI method has the following advantages:

⋆ simplicity of the method, solutions are always exist independently of the number of open shells;

⋆ it well describes "static" (avoided crossing of terms) and "nondynamic" electron correlations.

The disadvantages of the CI method are:

- it is badly working for large number of correlated electrons (when semi-empirical corrections on unselected determinants are large);

- unsmoothness of potential curves is a result of selection of determinants by some thresholds;

- the above semi-empirical energy corrections cannot be used when calculating other than spectroscopic properties.

V. THE COUPLED-CLUSTER APPROACHES

The complete space of $\{D_I\}$ is divided into two subspaces:

$\mathcal{M}_0$, model space, consists of small number (M) of the most important determinants $\{D_m\}_{m=1}^{M}$ to describe static and nondynamic correlations, which are taken into account exactly on $\mathcal{M}_0$;

$\mathcal{M}_0^{\perp}$, rest of space (usually very large), is included approximately to account for dynamic correlations (i.e. correlations at small interelectronic distances, "Coulomb holes").

The eigenstates of interest are presented as

$$|\Psi^{CC}\rangle \;=\; \sum_{m=1}^{M} C_m \mathbf{exp}[T^{(m)}]|D_m\rangle \;, \tag{18}$$

where $T^{(m)} \equiv T_1^{(m)} + T_2^{(m)} + \ldots$ is the cluster operator:

$$\begin{cases} T_1^{(m)} = \sum\limits_{i,a} \{\mathbf{a}_a{}^{+}\mathbf{a}_i\}\, t_{i.a}^{(m)} \;, \\ T_2^{(m)} = \frac{1}{2} \sum\limits_{ij,ab} \{\mathbf{a}_b{}^{+}\mathbf{a}_a{}^{+}\mathbf{a}_j\mathbf{a}_i\}\, t_{ij,ab}^{(m)} \;, \\ \cdots \;. \end{cases} \tag{19}$$

where $\mathbf{a}_a^{+}$ and $\mathbf{a}_i$ are the creation and annihilation operators (their combination $\mathbf{a}_a^{+}\mathbf{a}_i$ will replace the i-th one-electron state in the determinant by the a-th one). The coefficients $\{t_{i,a}^{(m)}, t_{ij,ab}^{(m)}\}$, etc. are called the cluster amplitudes and are calculated solving Bloch equations:

$$\mathbf{UHU} = \mathbf{HU} \;, \qquad (\mathbf{U} \equiv \sum_{m=1}^{M} \mathbf{exp}[T^{(m)}]|D_m\rangle\langle D_m|) \;. \tag{20}$$

The coefficients C_m and final energy E^{CC} are obtained from diagonalization of some effective Hamiltonian $\mathbf{H}^{\mathrm{eff}}$ on the model space:

$$\mathbf{H}^{\mathrm{eff}} \sum_{m=1}^{M} C_m|D_m\rangle = E^{CC} \sum_{m=1}^{M} C_m|D_m\rangle \;, \quad (\mathbf{H}_{nm}^{\mathrm{eff}} \equiv \langle D_n|(\mathbf{exp}[-T^{(m)}]\mathbf{H}\mathbf{exp}[T^{(m)}])|D_m\rangle) \;. \tag{21}$$

If all the $T_k^{(m)}$ are considered in the $T^{(m)}$ operator then the CC method is equivalent to the Full-CI one. However, in practical calculations, the third and following terms in $T^{(m)}$ (three-body and higher order cluster amplitudes) are usually neglected. Such a CC version is called CC-SD. There are three basic CC categories [18]:

- One-state or state-selective;
- Fock-space or valence universal methods;
- Hilbert-space or state-universal approaches.

The CC method has the following advantages:

⋆ It is the size-extensive method, i.e. the energy of the system is scaled properly with increase in the number of electrons (whereas the CI method is not size-extensive in a general case).

⋆ The CC-SD method takes into account the contributions not only from the determinants of the model space by applying the $(1+T_1^{(m)}+T_2^{(m)})$ operator but also approximately from all the rest determinants (whereas the CI method with the same number of unknown coefficients does not).

⋆ The CC method is one of the best methods for accounting the dynamic correlation.

The disadvantages of the CC method are:

- This is a nonvariational method, i.e. the CC energy is not an upper bound to the exact energy of the system (whereas the CI energy is).
- The CC equations are nonlinear and the effective Hamiltonian is non-Hermitian.
- Intruder states (i.e. such states from the $\mathcal{M}_0^{\perp}$ subspace, which are lying within the $\mathcal{M}_0$ subspace energy span) destroy the convergence of the CC iterations. Alleviation the problem is in using:
  - Incomplete model space procedures;
  - Energy shifting, RLE [19], DIIS [20, 21], IPM [22] procedures.

VI. SOME PRACTICAL CALCULATIONS

Calculations of the spectroscopic constants for the ground and lowest excited states of the HgH molecule and for the ground state of the HgH^+ ion were carried out with the help of the GRECP and relativistic CC methods in [23]. The results are within a few mbohr from the experimental data for bond lengths, tens of wave numbers for excitation energies and vibrational frequencies. It is demonstrated that the triple cluster amplitudes for the 13 outermost electrons and corrections for the Basis Set Superposition Errors (BSSE) [24, 25] are necessary to obtain accurate results for this molecule. The accurate GRECP/CI calculations of the spectroscopic constant for the ground state of the TlH molecule are presented in [26], in which the reliability of the semi-empirical energy corrections is in particular investigated.

The NOCR scheme was applied in the GRECP/CC calculations of the P,T-odd properties for the TlF molecule [14]. The corresponding GRECP/HF/NOCR results are in good agreement with the all-electron DHF results of other groups. Inclusion of electron correlation has changed the values on 20%. The previous NOCR version was employed in the GRECP calculations of the P,T-odd parameters and HFS constants for the YbF [27, 28] and BaF [29] molecules. A reasonable agreement with the experimental data for the HFS constants was attained. It was demonstrated that the spin-correlation effects of the unpaired electron with the deeply-lying outer core $5s$ and $5p$ shells should be taken into account in order to perform accurate calculations of the HFS and P,T-odd constants.

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TABLE I: Transition energies of the Tin (Z=50), Lead (Z=82) and Eka-lead (Z=114) atoms calculated by the DHF method with Coulomb and Coulomb-Gaunt two-electrons interaction for states with the ns^2np^2 configuration (in cm^{-1}).

Tin					
configuration	J	DC	DCG	absolute difference	relat. (%) difference
$(5s^2_{1/2}5p^2_{1/2})$	0	3113	3153	40	1.3
$(5s^2_{1/2}5p^1_{1/2}5p^1_{3/2})$	1	0	0	0	0
$(5s^2_{1/2}5p^1_{1/2}5p^1_{3/2})$	2	5143	5139	−4	−0.1
$(5s^2_{1/2}5p^2_{3/2})$	2	5941	5893	−48	−0.8
$(5s^2_{1/2}5p^2_{3/2})$	0	15873	15820	−53	−0.3
Lead					
configuration	J	DC	DCG	absolute difference	relat. (%) difference
$(6s^2_{1/2}6p^2_{1/2})$	0	0	0	0	0
$(6s^2_{1/2}6p^1_{1/2}6p^1_{3/2})$	1	4752	4644	−108	−2.3
$(6s^2_{1/2}6p^1_{1/2}6p^1_{3/2})$	2	9625	9514	−111	−1.2
$(6s^2_{1/2}6p^2_{3/2})$	2	18826	18592	−234	−1.2
$(6s^2_{1/2}6p^2_{3/2})$	0	28239	27995	−244	−0.9
Eka-lead					
configuration	J	DC	DCG	absolute difference	relat. (%) difference
$(7s^2_{1/2}7p^2_{1/2})$	0	0	0	0	0
$(7s^2_{1/2}7p^1_{1/2}7p^1_{3/2})$	1	27198	26806	−392	−1.4
$(7s^2_{1/2}7p^1_{1/2}7p^1_{3/2})$	2	30775	30391	−384	−1.2
$(7s^2_{1/2}7p^2_{3/2})$	2	66068	65225	−843	−1.3
$(7s^2_{1/2}7p^2_{3/2})$	0	74527	73674	−853	−1.1

TABLE II: HFS constants in the Indium (Z=49), Thallium (Z=81) and Eka-thallium (Z=113) atoms calculated by the DHF method with Coulomb and Coulomb-Gaunt interaction for different configurations (in MHz).

Indium				
configuration	DC	DCG	absolute difference	relat. (%) difference
$(5s^2_{1/2}5p^1_{1/2})$	1913	1900	−13	−0.7
$(5s^2_{1/2}5p^1_{3/2})$	288	287	−1	−0.3
$(5s^2_{1/2}5d^1_{3/2})$	4.41	4.40	−0.01	−0.2
$(5s^2_{1/2}5d^1_{5/2})$	1.88	1.88	0.0	0.0
$(5s^2_{1/2}6s^1_{1/2})$	1013	1011	−2	−0.2
Thallium				
configuration	DC	DCG	absolute difference	relat. (%) difference
$(6s^2_{1/2}6p^1_{1/2})$	18918	18691	−227	−1.2
$(6s^2_{1/2}6p^1_{3/2})$	1403	1391	−12	−0.9
$(6s^2_{1/2}6d^1_{3/2})$	20.8	20.8	0.0	0.0
$(6s^2_{1/2}6d^1_{5/2})$	8.72	8.70	−0.02	−0.2
$(6s^2_{1/2}7s^1_{1/2})$	7826	7807	−19	−0.2
Eka-thallium[a]				
configuration	DC	DCG	absolute difference	relat. (%) difference
$(7s^2_{1/2}7p^1_{1/2})$	150168	147538	−2630	−1.8
$(7s^2_{1/2}7p^1_{3/2})$	2007	1983	−24	−1.2
$(7s^2_{1/2}7d^1_{3/2})$	34.3	34.2	−0.1	−0.3
$(7s^2_{1/2}7d^1_{5/2})$	13.5	13.5	0.0	0.0
$(7s^2_{1/2}8s^1_{1/2})$	28580	28473	−107	−0.4

[a] The magnetic moment μ_N and spin I for the Eka-thallium nucleus were taken as those for Thallium. The presented results can be easily recalculated as only the proper values of μ_N and I are known because they just include the μ_N/I coefficient.

TABLE III: Transition energies between low-lying configurations of the eka-thallium (E113) atom derived from all-electron calculations and the errors of their reproducing in calculations with different RECP versions. All values are in cm^{-1}.

Configuration	All-el. DHFG[a]	21e-GRECP[b]	21e-RECP of Nash *et al.*[c]
	Transition energies	Absolute errors	
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}7p^1_{1/2}(J=1/2) \rightarrow$			
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}7p^1_{3/2}(J=3/2)$	25098	-23	282
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}8s^1_{1/2}(J=1/2)$	34962	0	-186
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}6f^1(nonrel.av.)$	50316	6	148
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}5g^1(nonrel.av.)$	52790	6	148
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}7d^1(nonrel.av.)$	45215	6	161
$6d^4_{3/2}6d^6_{5/2}7s^2_{1/2}(J=0)$	57180	6	148
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}7p^2_{1/2}(J=1/2)$	61499	32	4830
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}7p^1_{1/2}7p^1_{3/2}(rel.av.)$	83177	-4	5177
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}7p^2_{3/2}(rel.av.)$	112666	-9	5729
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}7p^1_{1/2}(rel.av.)$	115740	-2	5161
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}7p^1_{3/2}(rel.av.)$	149526	-10	5811
$6d^4_{3/2}6d^6_{5/2}7s^1_{1/2}(J=1/2)$	234385	-4	6151
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}7p^2_{1/2}(J=5/2)$	47410	403	-2389
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}7p^1_{1/2}7p^1_{3/2}(rel.av.)$	74932	341	-2089
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}7p^2_{3/2}(rel.av.)$	110435	306	-1556
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}7p^2_{1/2}(J=3/2)$	78862	375	-2272
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}7p^1_{1/2}7p^1_{3/2}(rel.av.)$	104097	405	-1968
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}7p^2_{3/2}(rel.av.)$	137083	473	-1436
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}7p^1_{1/2}(rel.av.)$	110139	380	-2317
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}7p^1_{3/2}(rel.av.)$	150116	338	-1679
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}7p^1_{1/2}(rel.av.)$	139841	439	-2184
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}7p^1_{3/2}(rel.av.)$	177157	506	-1541
$6d^4_{3/2}6d^5_{5/2}7s^2_{1/2}(J=5/2)$	239509	408	-1603
$6d^3_{3/2}6d^6_{5/2}7s^2_{1/2}(J=3/2)$	267208	579	-1431

[a]All-electron Dirac-Hartree-Fock-Gaunt (DHFG) calculation with Fermi nuclear charge distrtibution for $A=297$.

[b]GRECP generated in the present work from DHFG calculation.

[c]RECP from [30] (generated from DHF calculation without Gaunt iteraction).

TABLE IV: Transition energies between states of U (averaged over nonrelativistic configurations) derived from all-electron DHF calculations and the errors of their reproducing in calculations with different RECP versions. All values are in cm^{-1}.

	DHF	RECP of Ermler *et al.* [31]	Energy-adjusted PP[a]	SfC GRECP	Quadratic SfC GRECP	"Frozen core" (f^3)	"Frozen core" (f^2)
Num. of el-ns	All	14	32	24	24	24	24
Conf.	Tr.energy	Absolute error					
$5f^37s^26d^1 \rightarrow$							
$5f^37s^27p^1$	7383	387	-498	-35	-33	2	14
$5f^37s^2$	36159	332	130	4	6	3	16
$5f^37s^16d^2$	13299	-192	-154	-3	-5	-1	-16
$5f^37s^16d^17p^1$	17289	144	-621	-31	-31	-1	-5
$5f^36d^2$	54892	-121	-398	-14	-15	1	-21
$5f^37s^26d^1 \rightarrow$							
$5f^47s^2$	16483	176	788	-723	0	54	187
$5f^47s^2 \rightarrow$							
$5f^47s^16d^1$	15132	-738	-87	11	-11	-16	-35
$5f^47s^17p^1$	15016	90	-443	-37	-26	-1	-2
$5f^46d^2$	34022	-1287	-153	28	-13	-26	-62
$5f^46d^17p^1$	32341	-794	-457	-11	-23	-17	-39
$5f^37s^26d^1 \rightarrow$							
$5f^27s^26d^2$	3774	3096	-748	-17	-17	90	-96
$5f^27s^26d^2 \rightarrow$							
$5f^27s^26d^17p^1$	12646	-441	-626	-16	-15	-5	0
$5f^27s^26d^1$	42638	-498	155	24	25	-5	1
$5f^27s^16d^3$	10697	608	-240	-10	-10	13	1
$5f^27s^16d^27p^1$	19319	390	-826	-26	-26	6	0
$5f^37s^26d^1 \rightarrow$							
$5f^17s^26d^3$	29597	11666	-1526	-896	-104	466	48
$5f^17s^26d^3 \rightarrow$							
$5f^17s^26d^27p^1$	18141	-1367	-778	46	49	-2	-2
$5f^17s^26d^2$	49158	-1355	173	70	73	-3	-2
$5f^17s^16d^4$	7584	1655	-331	-39	-40	22	14
$5f^17s^16d^37p^1$	21154	779	-1055	-11	-11	16	10
$5f^37s^26d^1 \rightarrow$							
$5f^5$	100840	430	1453	-1860	22	105	291

[a]PseudoPotential (PP) from [32] (generated from all-electron calculation in the framework of Wood-Boring [33] approximation).